

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 299 004 B1

(12)

EUROPEAN PATENT SPECIFICATION(45) Date of publication of patent specification: **23.03.94** (51) Int. Cl.⁵: **A61L 31/00**(21) Application number: **88900458.6**(22) Date of filing: **29.12.87**(86) International application number:
PCT/FI87/00177(87) International publication number:
WO 88/05312 (28.07.88 88/17)

The file contains technical information submitted
after the application was filed and not included in
this specification

(54) **SURGICAL COMPOSITE AND USE OF A COMPOSITE FOR MANUFACTURING (PART OF) A DEVICE
FOR USE IN BONE SURGERY.**

(30) Priority: **13.01.87 FI 870111**(43) Date of publication of application:
18.01.89 Bulletin 89/03(45) Publication of the grant of the patent:
23.03.94 Bulletin 94/12(84) Designated Contracting States:
AT BE CH DE FR GB IT LI LU NL SE(56) References cited:
EP-A- 0 176 895
EP-A- 0 202 090
SE-B- 448 206
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Description

The invention relates to a surgical composite comprising a material selected from a resorbable (co)-polymer, said material containing oriented, at least partially fibrillated structural units which have been induced by drawing the material in solid state. The invention also relates to the use of a composite for manufacturing (part of) a device for use in bone surgery.

Surgical implants with good mechanical strength properties can be manufactured of resorbable polymeric materials (resorbable composites) which contain resorbable reinforcing elements. Resorbable or absorbable means in this connection that the material is metabolized by living tissues. Such resorbable materials and implants manufactured of them can be applied e.g. as rods, plates, screws, intramedullary nails etc. for fixation of bone fractures, osteotomies, arthrodesis or joint damages. An advantage of such implants and materials is that they are resorbed (depolymerized to cell nutrients) after the healing of the treated tissue. Therefore the resorbable implants, contrary to metallic implants in many cases, do not need a removal operation.

US-A-4 279 249 describes resorbable implant materials comprising polyglycolide fibres as reinforcement and polylactide as a binding polymer (as a resorbable matrix). EP-A-0 204 931 (FI 851828) describes self-reinforced resorbable materials, where the resorbable polymer matrix has been reinforced with resorbable reinforcement elements which have the same chemical element content as the matrix. Typical reinforcement elements in this connection are fibres or structures which have been constructed of them.

Further as to the state of the art, reference is made to EP-A-0 202 090 which discloses a tissue fastening device comprising a fastener member and a receiver member. The fastener member is made by forming an extruded, oriented filament and further annealing the formed filament. The surface of the fastener member is even.

US-A-4 141 087 refers to new polymers of isomorphous copolyoxalates to be used as surgical aids and prostheses. However, the polymers do not comprise oriented structural units embedded in a matrix of the same polymer. The products made by the method of US-A-4 141 087 are cast or machined non-reinforced resorbable prostheses which have only moderate mechanical strength properties.

The known resorbable materials reinforced with resorbable organic reinforcement elements have fairly high mechanical strength values. Therefore such materials can be applied in orthopaedics and traumatology in treatment of cancellous bone fractures, osteotomies, arthrodesis or joint damages. For example, the self-reinforced resorbable materials of EP-A-0 204 931 have bending strengths over 300 MPa (S. Vainionpää, Thesis, Helsinki 1987), which values clearly are higher than even the average strength values of cortical bone. Also the elastic moduli of known self-reinforced resorbable composites are quite high, typically of the order of magnitude of 10 GPa. So the strength values of these materials are clearly better than those of resorbable materials which have been manufactured by melt moulding techniques.

When one manufactures, using resorbable polymers, copolymers or polymer alloys, rods, profiles, plates etc. implants by melt moulding techniques like by injection moulding or by extrusion, the mechanical properties of the products remain on the level which is typical for thermoplastic polymers. The strength values (like tensile, shear and bending strength) typically do not exceed the value 150 MPa showing typically strength values between 40 and 80 MPa and moduli between 1 and 6 GPa. The reason for this behaviour is the fact that the flow orientation which exists in the flowing polymer melt is relaxed as a consequence of molecular thermal movements when the melt moulded sample is cooled. When it is a question of a crystallizable polymer, the sample is crystallized to partially crystalline, spherulitic structure. So the polymeric material manufactured by melt moulding typically consists of folded crystalline lamellae (thickness 100-300 Å; width about 1 µm), which are surrounded by the amorphous polymer. On the other hand, the lamellae can be thought to consist of mosaic-like folded blocks (width some hundreds of Å). The lamellae as a rule form ribbon-like structures, which grow from crystallization centres, so-called nuclei, to three-dimensional spherical spherulitic structures. Because the polymer material which has been crystallized with the spherulitic mechanism does not show as a rule significant orientation of polymer molecules with strong covalent bonds, its mechanical strength values remain on the above mentioned level. Molecular orientation can only remain on the surface of the sample because of rapid cooling in the mould (as in the case of injection moulding).

Although the reinforced resorbable composites show considerably better strength properties than melt moulded resorbable composites, it is often necessary to manufacture quite big implants, like rods, intramedullary nails, screws or plates of resorbable reinforced composites. This is necessary because one must secure for the load carrying capacity (e.g. bending or shear load carrying capacity) of the implants a security marginal high enough to confirm the stability of the fixation also in such a case when outer stresses or muscle stresses are directed to the fixated fracture, osteotomy, arthrodesis or joint damage, because the

above mentioned stresses can clearly exceed the weight of the patient. On the other hand, such big implants required by the security of the patient, cause quite heavy operative traumas to the bone tissue and/or to the soft tissues when the implant e.g. is located into a drill-hole which has been drilled into the bone, or the implant is fastened on the surface of the bone. With the increasing size of the implant, the possibilities of a foreign body reaction increase, the reaction may grow stronger or its duration may be prolonged because the implant and the resorption of the implant cause physical and chemical stresses to the living tissues which are in a direct correlation to the size of the implant.

So far, the elastic modulus values of resorbable implants which have been manufactured of organic materials are at the best in the order of magnitude of 10 GPa. This is a lower level of elastic modulus than the elastic moduli of cortical bones, which are typically in the order of magnitude of 20 GPa and can even exceed 30 GPa. When the main goal of the surgeon is as good a fixation as possible it is advantageous when the elastic modulus of the implant approximates the elastic modulus of the bone as much as possible. In the ideal case the elastic moduli of the bone to be operated and of the implant are equal. Therefore it is evident that an efficient fixation of cortical bone, e.g. long bones, requires resorbable organic composite materials which have higher elastic modulus values than those of the known materials.

In this invention we have unexpectedly found that in connection with increased strength and elastic modulus values of resorbable polymeric composite by orientation of the molecular structure of the material in such a way that it is at least partially fibrillated, it is advantageous to provide the surface of the device made of the composite with a profiled structure which includes said fibrillated structural units.

Thus the inventive new macroscopical resorbable self-reinforced implant materials have considerably higher strength and elastic modulus values than those of the known resorbable implant materials. When the materials of this invention are applied as surgical fixation devices or when such devices are manufactured from said materials one can effectively decrease the operative trauma which the implant causes and at the same time one can obtain significantly better fixation than with the known materials. This invention describes at least partially fibrillated (a) fixation materials for treatment of bone fractures, osteotomies, arthrodesis or joint damages, (b) materials for reconstruction and augmentation of bone tissue and (c) fixation devices, reconstruction devices and augmentation devices like rods, plates, screws, intramedullary nails, clamps and chutes manufactured at least partially of the above materials using as raw material resorbable polymer, copolymer or polymer mixture.

Further this invention describes the use of at least partially fibrillated resorbable materials and especially the use of rods, plates, screws, intramedullary nails, clamps or chutes manufactured of the above mentioned materials in fixation of bone fractures, osteotomies, arthrodesis or joint damages or in augmentation or reconstruction of bone tissue.

This invention is more closely explained in the following specification with simultaneous references to the annexed drawings, in which

Fig. 1a shows schematically the transformation of a lamellar structure to a fibrillar structure,

Fig. 1b shows schematically the molecular structure inside and between the microfibrils,

Fig. 1c shows schematically the structure of the fibrillated polymer,

Fig. 2 shows schematically the overall construction of a composite material,

Fig. 3 shows schematically the structural units of the fibrillated structure of polymer fibers,

Fig. 4 shows schematically some of net structures which can be made of the composite,

Fig. 5 shows schematically a chute embodiment of the composite,

Fig. 6 shows schematically the use of the chute of Fig. 5 in connection with the surgery related to the alveolar ridge,

Figs. 7a and 7b show the construction and the behaviour of the rod used in the test of the Example 5, and

Figs. 8a-c show the construction of the implant in connection with Example 8.

The orientation and fibrillation of spherulitic polymer systems is a process, which has been studied extensively in connection with the manufacturing of thermoplastic fibres. For example, US-A-3 161 709 describes a three phase drawing process, where the melt moulded polypropylene filament is transformed to a fibre with high mechanical tensile strength.

The mechanism of the fibrillation is of its main features the following one (C.L. Choy *et al.* Polym. Eng. Sci., 23 1983, p. 910). When a semicrystalline polymer is drawn, the molecular chains in the crystalline lamellae are aligned rapidly along the draw direction. At the same time, the spherulites are elongated and finally broken up. Crystalline blocks are torn off from the lamellae and are connected by taut tie-molecules originating from partial unfolding of chains. The alternating amorphous and crystalline regions, together with the taut tie-molecules, therefore form long, thin (ca. 100 Å width) microfibrils which are aligned in the draw direction. Since the intrafibrillar tie-molecules are created at the interfaces between crystalline blocks, they

lie mainly on the outside boundary of microfibrils. Tie-molecules which linked different lamellae in the starting isotropic material are now connecting different microfibrils, i.e., they become interfibrillar tie-molecules locating at the boundary layers between adjacent microfibrils.

Figure 1a shows schematically how a group of lamellae is transformed to a fibrillar structure (to a fibril which comprises a group of microfibrils) as a consequence of drawing and Figure 1b shows schematically the molecular structure inside microfibrils and between them. Figure 1c shows schematically the structure of fibrillated polymer. This Figure shows several fibrils (one of them has been coloured grey for clarity) which comprise several microfibrils with the length of several micrometres.

The fibrillar structure is already formed at relatively low draw ratios λ (where λ = the length of the sample after drawing/the length of the sample before drawing). E.g. HD-polyethylene is clearly fibrillated with the λ value of 8 and polyacetal (POM) with the λ value of 3.

When the drawing of the fibrillated structure is further continued (this stage of the process is often called ultra-orientation), the fibrillar structure is deformed by shear displacement or microfibrils, giving rise to an increase in the volume fraction of extended interfibrillar tie-molecules. If the drawing is performed at high temperature, the perfectly aligned tie-molecules will be crystallized to form axial crystalline bridges connecting the crystalline blocks.

The excellent strength and elastic modulus values of the fibrillated structure are based on the strong orientation of polymer molecules and molecular segments into the direction of the drawing (into the direction of the long axis or microfibrils).

Regardless of the high tensile strength of fibrillated fibres, they cannot be applied as fixation devices of bone fractures, osteotomies, arthrodesis or joint damages, because thin fibres are flexible and therefore they do not show macroscopical bending strength and bending modulus and because of their small cross-sectional area they do not have the necessary shear load carrying capacity which the macroscopical fixation device must have.

Fibrillation of macroscopical polymeric samples, like rods and tubes, is known earlier in the case of biostable polyacetal and polyethylene (see e.g. K. Nakagawa and T. Konaka, Polymer 27, 1986, p. 1553 and references therein). However, the fibrillation of macroscopical samples of resorbable polymers has not been known earlier.

At least partial fibrillation of a macroscopical polymer sample can be carried out e.g. by cooling in a capillary tube flowing polymer melt rapidly to the solid state in such a way that the molecular orientation of the flowing molecules cannot relax as a consequence of molecular motions to a total or partial state of random orientation.

Stronger fibrillation and therefore also better mechanical properties can be achieved by a mechanical deformation (orientation) of macroscopical polymer samples. Such a mechanical deformation is usually done by drawing or by hydrostatic extrusion of material in such a physical condition (in solid state), where strong molecular structural changes of crystalline structure and amorphous structure to fibrillar state are possible. As a consequence of fibrillation the resorbable polymeric material which has been manufactured e.g. by the injection moulding or extrusion and which material initially has a mainly spherulitic crystalline structure, changes first partially and later on totally to a fibrillated structure which is strongly oriented in the direction of drawing or of hydrostatic extrusion. Such a resorbable material consists among other things of oblong crystalline microfibrils and of tie-molecules connecting microfibrils and of oriented amorphous regions. In a partially fibrillated structure the amorphous regions between microfibrils form a more significant part of the material than in an ultraoriented material where in the extreme case amorphous material exists only as crystal defects around the ends of the polymer molecule chains. When the degree of fibrillation increases in a material its strength and elastic modulus values increase many times in comparison to the same values of non-fibrillated material.

Known resorbable composite materials typically comprise randomly oriented (non-oriented) binding material phase (matrix), which binds to each other reinforcing elements like fibres which have strongly oriented internal structure. Such a structure has been shown schematically in Figure 2, where oriented and non-oriented molecular chains or their parts have been illustrated with thin lines. The strength properties of the binding phase are significantly weaker than the strength properties of the reinforcement elements. Therefore the strength properties of the composite in the direction of orientation of reinforcement elements increase when the amount of reinforcement elements in the material is increased. As a consequence of practical difficulties the amount of reinforcement elements cannot exceed ca. 70 weight-% of the weight of the composite. Therefore the strength properties of reinforcement elements cannot be utilized totally, because the composite contains also the weaker matrix material, which also contributes to the total strength of the composite.

By means of orientation and fibrillation it is possible to manufacture self-reinforced composites of resorbable polymers, copolymers and polymer alloys, where nearly the whole mass of material has been oriented in a desired way and where the amount of the amorphous phase is small. Therefore these materials show very high mechanical strength properties in the direction of orientation: tensile strength even 1000-1500 MPa and elastic modulus 20-50 GPa. Accordingly, these strength values are clearly better than those of known resorbable composites and even about ten times higher than the strength values of melt moulded resorbable materials.

Figure 3 shows schematically the following structural units which can be seen in the fibrillated structure of polymer fibres and also in the structure of macroscopical, fibrillated polymer samples like rods and tubes: crystalline blocks which are separated from each other by amorphous material (e.g. free polymer chains, chain ends and molecular folds), tie-molecules, which connect crystalline blocks with each other (the amount and thickness of tie-molecules increases with increasing draw ratio λ) and possible crystalline bridges between crystalline blocks. Bridges can be formed during drawing when tie-molecules are oriented and grouped themselves to bridges (C.L. Choy *et al.* J. Polym. Sci., Polym. Phys. Ed., 19, 1981, p. 335-352).

The oriented fibrillated structure which is shown in Figures 1 and 3 develops already at so-called natural draw ratios 3-8. When the drawing is continued after this as an ultraorientation at a high temperature, the quantity of crystalline bridges can increase very highly and in the extreme case bridges and crystalline blocks form a continuous crystalline structure. The effects of tie-molecules and bridges are often similar and therefore their exact discrimination from each other is not always possible.

Orientation and fibrillation can be characterized experimentally by means of several methods. The orientation function f_c , which can be measured by means of x-ray diffraction measurements, characterizes the orientation of molecular chains of the crystalline phase. As a rule, the f_c attains already at natural drawing ratios ($\lambda < 6$) the maximum value 1. The polymeric material with spherulitic structure shows $f_c < 1$.

Birefringence which can be measured by means of polarization microscope is also a characteristic, which describes molecular orientation of molecular chains. As a rule it grows strongly at natural draw ratios ($\lambda < 6$) and thereafter during ultraorientation more slowly, which shows that the molecular chains of the crystalline phase are oriented into the drawing direction at natural draw ratios and the orientation of molecules in the amorphous phase continues further at higher draw ratios (C.L. Choy *et al.* Polym. Eng. Sci., 23, 1983, p. 910-922).

The formation of the fibrillated structure can be shown in many cases illustratively by studying the fibrillated material by means of optical and/or electron microscopy (see e.g. T. Konaka *et al.* Polymer, 26, 1985, p. 462). Even single fibrils which consist of microfibrils can be seen clearly in scanning electron microscopy figures which are taken of the fibrillated structure.

Table 1 shows some known resorbable polymers, which can be applied in manufacturing of resorbable materials and devices of this invention. A presupposition to an efficient fibrillation is, however, that the polymer exists in a partially crystalline form. Therefore such polymers, which because of their physical structure (e.g. configuration state) are not crystallizable, cannot be effectively fibrillated.

Table 1. Resorbable polymers

| | |
|----|---|
| 5 | <u>Polymer</u> |
| | Polyglycolide (PGA) |
| | Copolymers of glycolide: |
| | Glycolide/L-lactide copolymers (PGA/PLLA) |
| 10 | Glycolide/trimethylene carbonate copolymers (PGA/TMC) |
| | Poly lactides (PLA) |
| | Stereocopolymers of PLA: |
| | Poly-L-lactide (PLLA) |
| 15 | Poly-DL-lactide (PDLLA) |
| | L-lactide/DL-lactide copolymers |
| | Copolymers of PLA: |
| | Lactide/tetramethylglycolide copolymers |
| 20 | Lactide/trimethylene carbonate copolymers |
| | Lactide/ δ -valerolactone copolymers |
| | Lactide/ ϵ -caprolactone copolymers |
| | Polydepsipeptides |
| | PLA/polyethylene oxide copolymers |
| 25 | Unsymmetrically 3,6-substituted poly-1,4-dioxane-2,5-diones |
| | Poly- β -hydroxybutyrate (PHBA) |
| | PHBA/ β -hydroxyvalerate copolymers (PHBA/HVA) |
| 30 | (continues) |

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Poly- β -hydroxypropionate (PHPA)
 Poly-p-dioxanone (PDS)
 Poly- δ -valerolactone
 5 Poly- ϵ -caprolactone
 Methylmethacrylate-N-vinyl pyrrolidone copolymers
 Polyesteramides
 10 Polyesters of oxalic acid
 Polydihydropyrans
 Polyalkyl-2-cyanoacrylates
 Polyurethanes (PU)
 15 Polyvinylalcohol (PVA)
 Polypeptides
 Poly- β -malic acid (PMLA)
 20 Poly- β -alkanoic acids

Reference: P. Törmälä, S. Vainionpää and P. Rokkanen in
 25 IVA's Beijer Symposium "Biomaterials and Biocompatibility",
 Stockholm, Sweden, August 25-26, 1987.

At least partially fibrillated and especially ultraoriented, resorbable polymer materials are a particularly
 30 advantageous special case of oriented, self-reinforced resorbable composite materials where the oriented
 reinforcement elements (crystalline blocks, tie-molecules and crystalline bridges) form and/or group them-
 selves during the mechanical deformation and where the phase which binds the above mentioned structural
 units is formed among other things of the following structural elements: amorphous phase, the interfaces
 35 between crystalline blocks and the interfaces between crystalline bridges and microfibrils, which structural
 elements are also typically oriented strongly in the direction of deformation.

The resorbable, at partially fibrillated implant materials and osteosynthesis devices of this invention can
 be formed to different kind of fixation devices like screws, rods with scaly covering and other profiled
 structures and clamps or other bended structures, because in this invention it has unexpectedly been found
 40 that the oriented resorbable materials can be hot-worked mechanically at high temperatures without losing
 the fibrillated structure. This makes possible e.g. the manufacturing of especially strong and tough screws
 of the at least partially fibrillated rods of this invention.

It is natural that fibrillated resorbable materials can contain additionally different kinds of additives or
 auxiliary materials to make the processing of the material more easy (e.g. stabilizers, antioxidants or
 plasticizers) or to change its properties (e.g. plasticizers or powder-like ceramic materials) or to make its
 45 handling more easy (e.g. colours).

The stiff and strong resorbable fixation materials of this invention can be applied in the form of rods,
 plates or other profiles also in the manufacture of bigger fixation devices as reinforcement elements for
 example by packing into a cylindrical, oblong injection moulding mould fibrillated rods and by filling the
 mould then by injecting into it suitable resorbable matrix polymer melt. When the injection is carried out
 50 from one end of the oblong mould, the injected melt flows in the direction of resorbable reinforcement
 elements. When the matrix material (polymer melt) flows and solidifies rapidly, an advantageous orientation
 is formed into it in the direction of the reinforcement elements.

The stiff and strong fixation rods or plates of this invention can be used also to construct stiff net-like
 and plate-like structures, which can resemble of their mechanical properties more metallic nets than nets
 55 which are manufactured of organic textile fibres. Figure 4 shows schematically some types of net structures
 which are constructed of stiff, strong resorbable rods. Part of the rods has been described as white and part
 as black for sake of clarity. Such nets can be applied as such e.g. to treatment of comminuted fractures by
 combining the comminuted parts of broken bone to each other and by bending the net around the parts of

broken bone to support it and by fixing the net e.g. with resorbable sutures or clamps. Nets of this invention can be manufactured also e.g. by hot-pressing them to curved plates, chutes or box-like etc. corresponding structures, which can be applied to the reconstruction of bone etc. in such a way that a defect in bone tissue (a hole, a cavity, a cyst, etc.) is filled with tissue compatible ceramic powder like hydroxyapatite or tricalciumphosphate and the curved net is fixed on the defect to a cover, which immobilizes ceramic particles and prevents their movement from the defect. Because the nets of this invention are stiff they function in this connection as significantly more effective immobilizers than the known flexible nets which are manufactured of resorbable fibres.

Figure 5 shows schematically a net structure of this invention which is manufactured of resorbable rods and which has been bended to the form of a chute e.g. by hot pressing. Such a chute can be applied advantageously with ceramic materials to augmentation of bone tissue of alveolar ridges in the following way. First the subperiosteal tunnel is made surgically below the gingival tissue on the surface of the alveolar ridge. The resorbable tube is pushed inside of the tunnel in such a way that the convex surface of the chute is directed towards the gingival tissue and the end surfaces of the sides of the chute are placed on the alveolar ridge. This situation has been described schematically in Figure 6 in the case of an operation which is done to the right side of the mandible. After installation of the chute it can be filled with ceramic bone graft powder and after that the operation incision can be closed. If necessary, it is possible to place on the same alveolar ridge several chutes after another. Such a chute prevents the movements of ceramic powder which has been packed below it. At the same time bone and connective tissue cells grow from the bone tissue of alveolar ridge and from the surrounding soft tissues into the ceramic powder by immobilizing it at last to a part of the bone tissue of alveolar ridge. The resorbable chute is resorbed at the same time or later.

Ceramic powders and pieces can be applied also in many other ways to augmentation or reconstruction of bone tissue (as bone graft materials).

Ceramic materials (bioceramics), which are tissue compatible and/or which form chemical bonds with bone tissue and/or which promote the growth of bone tissue, are e.g. calciumphosphate: apatites like hydroxyapatite, HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (R.E. Luedemann *et al.*, Second World Congress on Biomaterials (SWCB), Washington, D.C., 1984, p. 224), trade names like Durapatite, Calcitite, Alveograf and Permagraft; fluoroapatites; tricalciumphosphates (TCP) (e.g. trade name Synthograft) and dicalciumphosphates (DCP); magnesiumcalciumphosphates, β -TCMP (A. Ruggeri *et al.*, Europ. Congr. on Biomaterials (ECB), Bologna, Italy, 1986, Abstracts, p. 86); mixtures of HA and TCP (E. Gruendel *et al.*, ECB, Bologna, Italy, 1986, Abstracts, p. 5, p. 32); aluminiumoxide ceramics; bioglasses like SiO_2 -CaO- Na_2O - P_2O_5 , e.g. Bioglass 45S (structure: SiO_2 45 wt-%, CaO 24,5 %, Na_2O 24,5 % and P_2O_5 6 %) (C.S. Kucheria *et al.*, SWBC, Washington, D.C., 1984, p. 214) and glass ceramics with apatites, e.g. MgO 4,6 wt-%, CaO 44,9 %, SiO_2 34,2 %, P_2O_5 16,3 % and CaF 0,5 % (T. Kokubo *et al.*, SWBC, Washington, D.C., 1984, p. 351) and calciumcarbonate (F. Souyris *et al.*, ECB, Bologna, Italy, 1986, Abstracts, p. 41).

The applications of the above ceramic materials as synthetic bone grafts have been studied by different means by using them for example both as porous and dense powder materials and as porous and dense macroscopical samples as bone grafts. Also ceramic powder - polymer composites have been studied in this means (e.g. W. Bonfield *et al.* SWBC, Washington, D.C., 1984, p. 77).

The resorbable strong and stiff materials of this invention can be applied in many different ways combined with porous bioceramics to biocomposites. The mechanical properties, especially the impact strength, bending strength and shear strength of such composites are significantly better than the corresponding properties of porous bioceramics. US-A-4 863 741 (FI 863573) describes several possibilities to combine resorbable polymeric materials and bioceramics. Those principles can be applied also when the materials of this invention are used in combination with bioceramics.

This invention has been illustrated by means of the following examples.

EXAMPLE 1.

Poly-L-lactide (PLLA) ($M_w = 600.000$) was injection moulded to cylindrical rods with a diameter (\varnothing) 4 mm. The rods were drawn to the drawing ratio $\lambda = 7$ at temperatures from room temperature to $T_m - 40^\circ\text{C}$ (where T_m = the melting point of the polymer). The fibrillated structure of the drawn rods was seen microscopically. Part of the rods was drawn further to a drawing ratio $\lambda = 12$ (ultraorientation). As reference samples were sintered self-reinforced rods ($\varnothing = 1.5$ mm) of PLLA fibres (tensile strength 800 MPa, $\varnothing = 15$ μm) which rods were manufactured by a method described in EP-A-0 204 931 (FI Pat. Appl. 851828).

Following strength values were measured for the injection moulded, fibrillated and sintered self-reinforced rods: tensile strength, elastic modulus and shear strength. The results of measurements are

given in Table 1.

Table 1

| Strength properties of PLLA rods | | | | | |
|----------------------------------|--|--------------------|------------------------|------------------------|----------------------|
| Sample No. | Manufacturing method | Rod thickness (mm) | Tensile strength (MPa) | Elastic strength (GPa) | Shear strength (MPa) |
| 1 | Injection moulding | 4 | 80 | 5.5 | 70 |
| 2 | Injection moulding + fibrillation ($\lambda = 7$) | 1.4 | 560 | 14 | 360 |
| 3 | Injection moulding + fibrillation ($\lambda = 12$) | 1.2 | 800 | 17 | 470 |
| 4 | Self-reinforcing (sintering) | 1.5 | 400 | 10 | 260 |

Table 1 shows that the strength properties of the fibrillated, resorbable rods of this invention are clearly better than the strength properties of the known resorbable materials.

EXAMPLE 2.

Resorbable rods of Example 1 (length 25 mm) were applied to fixation of the arthrodesis of the proximal phalanx of thumb by removing the both joint surfaces, by joining the uncovered bone surfaces temporarily to each others by clamps to an arthrodesis surface, by drilling through the arthrodesis surface two drilling channels and by tapping into the drilling channels the resorbable fixation rods. 20 patients were operated. The average area of the arthrodesis surfaces was ca. 170 mm². The calculatory shear load carrying capacity of the fixation was 1100 N, when two fibrillated rods No. 2 were applied. The proportion of drill channels (which describes the operative trauma) of the arthrodesis surface was 1.8 %. The corresponding values were for fibrillated rods No. 3 1060 N and 1.3 % and for sintered rods No. 4 920 N and 2.1 %. Accordingly the fibrillated rods give a stronger fixation than the sintered rods. Also the operative trauma was smaller in the case of the fibrillated rods. Injection moulded rods were not applied in fixation, because they should have caused clearly bigger operative trauma (ca. 15 %) than the other materials.

EXAMPLE 3.

Injection moulding was applied to manufacture rods ($\phi = 3.2$ mm) of the following resorbable polymers: polyglycolide (PGA) ($M_w = 100.000$), glycolide/lactide copolymer (PGA/PLA, the molar ratio 87/13, $M_w = 120.000$), poly- β -hydroxybutyrate (PHBA) ($M_w = 500.000$) and poly-p-dioxanone (PDS) ($M_w = 300.000$).

Polarization microscopy and scanning electron microscopy showed that, exclusive of a thin surface layer, the rods had a spherulitic crystalline structure. The melting points (T_m) of the materials of the rods were measured by differential scanning calorimetry (DSC) and the following values were obtained for T_m : PGA (225°C), PGA/PLA (180°C), PHBA (175°C) and PDS (110°C). The tensile strengths of the rods were: PGA (60 MPa), PGA/PLA (50 MPa), PHBA (30 MPa) and PDS (40 MPa). The rods were fibrillated by drawing them at temperatures from room temperature to $T_m - 10^\circ\text{C}$ to drawing ratios $\lambda = 8-16$. The diameters of the fibrillated rods were between 0.8 mm and 1.1 mm. The tensile strengths of the fibrillated rods were: PGA (600 MPa), PGA/PLA (550 MPa), PHBA (400 MPa) and PDS (300 MPa).

EXAMPLE 4.

Fibrillated PGA rods of Example 3 and self-reinforced, sintered rods ($\phi = 1.1$ mm; manufactured of PGA sutures with trade name Dexon, size 3-0) which were 50 mm long, were hydrolyzed at 37°C in distilled water for 5 and 7 weeks. The shear load carrying capacities of fibrillated (f) and sintered (s) rods were after manufacturing f: 570 N and s: 300 N. After hydrolysis of 5 weeks the corresponding values were f: 160 N and s: 30 N. After 7 weeks hydrolysis the sintered rods had already lost their shear load carrying capacity, but the fibrillated rods showed still 75 N shear load carrying capacity.

EXAMPLE 5.

Fibrillated PGA rods of Example 3 (length 50 mm, \varnothing 1.1 mm) were bended in a mould to clamps shown schematically in Figure 7a in a bending temperature of 180°C. Corresponding self-reinforced clamps were manufactured of PGA sutures (trade name Dexon, size 3-0) by sintering them according to the method of EP-A-0 204 931 (FI 851828) at elevated temperature and pressure in a clamp mould. The tensile load carrying capacity of fibrillated and sintered clamps was measured by fixing the 10 mm long arms of clamps into holes which were in drawing jaws of a tensile testing machine and by drawing the clamps according to Figure 7b. The clamps were broken typically according to Figure 7b from the base of the arm. The fibrillated clamps of this invention showed mean tensile load carrying capacity of 300 N and the sintered clamps a corresponding value of 120 N.

EXAMPLE 6.

Fibrillated PLLA rods No. 4 of Example 1 were compression moulded in a mould with a screw-like mould cavity at about 160°C temperature to resorbable 30 mm long screws, with the core thickness of 1.1 mm and the height of threads 0.5 mm and the distance between the threads 0.8 mm. The tensile load carrying capacity of the screws was 300 N. The corresponding screws which were manufactured by injection moulding of PLLA showed a tensile load carrying capacity of 80 N and the corresponding self-reinforced, sintered rods which were manufactured of PLLA fibres of Example 1 showed a tensile load carrying capacity of 150 N.

EXAMPLE 7.

Fibrillated PLLA rods No. 3 (length 60 mm, \varnothing 1.2 mm) of Example 1 were coated with PDLLA ($M_w = 100.000$) by immersing the rods in a 5 % acetone solution of PDLLA and by evaporating the solvent. The operation was repeated so many times that the rods had at last 40 w-% of PDLLA. The coated rods were compressed in a cylindrical mould (the length 60 mm and \varnothing 4.5 mm) at 160°C to cylindrical resorbable rods which showed a bending strength of 450 MPa and a bending modulus of 14 MPa.

EXAMPLE 8.

Porous hydroxyapatite (HA) rods (open porosity about 50 %, $\varnothing = 4$ mm and length 60 mm), which contained on their outer surface 6 longitudinal grooves shown schematically in Figure 8a and in a crosssectional Figure 8b (the cross-section plane A-A of Figure 8a), and resorbable reinforcing materials of this invention were applied to manufacture biocomposite rods (intramedullary nails). The used reinforcing element materials were fibrillated PLLA rods (length 60 mm, \varnothing 1.0 mm) of Example 1. Also PLLA fibre bundles coated with PDLLA (ca. 0.1 mm thick, slightly twisted bundle of fibres; \varnothing of single fibres 15 μ m and tensile strength 800 MPa) were applied as shown below. A 5 % (w/v) acetone solution of PDLLA ($M_w = 100.000$) was spread to the grooves of HA rods and the fibrillated resorbable rods which were immersed in the same solution were pushed into the grooves. The rods were adhered into the grooves when acetone was evaporated. HA rods with the fibrillated PLLA rods in their grooves were coated with PLLA fibre bundle (coated with PDLLA) by filament winding method. The filament winding was carried out at 150°C temperature in such a way that the HA rods were coated with several fibre bundle layers with different directions so that the fibre bundle layer was at the most 0.4 mm thick. The filament winding was carried out in such a way that between fibre bundles remained areas of rod surface without fibres. These uncovered areas of HA rods could be seen on the surface of biocomposite rods as is shown schematically in Figure 8c. The resorbable reinforced coating of rods was pressed smooth in a cylindrical mould ($\varnothing = 5.0$ mm). These biocomposites showed a bending strength of 140 MPa, when the bending strength of mere HA rods was 12 MPa.

The above biocomposite rods were applied to fixation of osteotomies of rabbit femur in the following way. The osteotomy was done with a diamond saw to the uncovered proximal part of rabbit femur about 1 cm from the neck of the femur. The osteotomy was fixed with clamps. A drill hole ($\varnothing = 5$ mm) was drilled through the greater trochanter vertically into the intramedullary channel of femur. The biocomposite rod was tapped into the drill hole so that the upper end of the rod was located on the level of the bone surface. The clamps were removed and soft tissues were closed with a resorbable suture. The animals were returned to their cages and after anesthesia they could immediately move freely. 20 test animals were used. The follow-up time of 6 months showed that all the osteotomies were healed well. Histological examinations of

bone-biocomposite test samples showed growth of bone tissue from femoral bone into the open porosity of HA rods.

Claims

- 5 1. Surgical composite comprising a material selected from a resorbable (co)polymer, said material containing oriented, at least partially fibrillated structural units which have been induced by drawing the material in solid state, **characterized** in that the composite is a device for use in bone surgery or forms part thereof, wherein at least the surface of the device has a profiled structure which includes
10 said fibrillated structural units.
2. Surgical composite according to claim 1, **characterized** in that the profiled structure contains at least partially ultraoriented structural units.
- 15 3. Surgical composite according to claims 1 and 2, **characterized** in that the profiled structure shows a shear strength value of at least 200 MPa and a shear modulus value of at least 4 GPa.
4. Surgical composite according to claims 1 and 2, **characterized** in that profiled structure shows a bending strength value of at least 200 MPa and a bending modulus value of at least 4 GPa.
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5. Surgical composite according to any of claims 1-4, **characterized** in that it has been constructed to net-like structures.
6. Surgical composite according to claim 5, **characterized** in that the net-like structures have been
25 formed to formed pieces like curve nets and chutes.
7. Use of a composite comprising a material selected from a resorbable (co)polymer, said material containing oriented, at least partially fibrillated structural units which have been induced by drawing the material in solid state, for manufacturing (part of) a device for use in bone surgery, wherein at least the
30 surface of said device or of said part has a profiled structure which includes said fibrillated structural units.

Patentansprüche

- 35 1. Komposit für chirurgische Zwecke, für welches als Material ein resorbierbares (Co)Polymer ausgewählt worden ist, welches ausgerichtete, mindestens teilweise eine faserige Struktur aufweisende Baueinheiten enthält, die durch Strecken des festen Materials hervorgerufen wurde, dadurch gekennzeichnet, dass das Komposit eine Anordnung ist oder einen Teil einer Anordnung bildet, welche in der Knochenchirurgie Anwendung findet, wobei mindestens die Oberfläche der Anordnung eine profilierte
40 Struktur aufweist, in der die genannten Baueinheiten mit faseriger Struktur enthalten sind.
2. Komposit nach Anspruch 1, dadurch gekennzeichnet, dass die profilierte Struktur Baueinheiten mit mindestens teilweiser Ultraausrichtung aufweist.
- 45 3. Komposit nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, dass die profilierte Struktur eine Schubfestigkeit von mindestens 200 MPa aufweist und einen Schubmodul von mindestens 4 GPa hat.
4. Komposit nach den Ansprüchen 1 und 2, dadurch gekennzeichnet, dass die profilierte Struktur eine Biegefestigkeit von mindestens 200 MPa aufweist und einen Biegemodul von mindestens 4GPa hat.
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5. Komposit nach einem der Ansprüche 1-4, dadurch gekennzeichnet, dass es zu einem netzartigen Gebilde geformt ist.
6. Komposit nach Anspruch 5, dadurch gekennzeichnet, dass aus dem netzartigen Gebilde gekrümmte
55 Netze oder Rinnen geformt sind.
7. Verwendung eines Komposits, für welches als Material ein resorbierbares (Co)Polymer ausgewählt worden ist, welches ausgerichtete, mindestens teilweise eine faserige Struktur aufweisende Baueinhei-

ten enthält, die durch Strecken des festen Materials hervorgerufen wurde, um daraus einen Teil einer Anordnung oder eine ganze Anordnung zur Anwendung in der Knochenchirurgie herzustellen, wobei mindestens die Oberfläche des Teiles oder der Anordnung eine profilierte Struktur aufweist, in welcher die Baueinheiten mit faseriger Struktur enthalten sind.

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Revendications

1. Composite chirurgical comprenant une matière choisie parmi les (co)polymères pouvant se résorber, ladite matière contenant des unités constitutives orientées, au moins partiellement fibrillées, qui ont été produites par un étirage de la matière à l'état solide, caractérisé en ce que le composite est un dispositif ou forme une partie d'un dispositif à employer en chirurgie osseuse, dans lequel au moins la surface du dispositif a une structure profilée qui comprend lesdites unités constitutives fibrillées.
2. Composite chirurgical selon la revendication 1, caractérisé en ce que la structure profilée contient des unités constitutives au moins partiellement ultraorientées.
3. Composite chirurgical selon les revendications 1 et 2, caractérisé en ce que la structure profilée présente une valeur de résistance au cisaillement d'au moins 200 MPa et une valeur du module de cisaillement d'au moins 4 GPa.
4. Composite chirurgical selon les revendications 1 et 2, caractérisé en ce que la structure profilée présente une valeur de résistance à la flexion d'au moins 200 MPa et une valeur du module de flexion d'au moins 4 GPa.
5. Composite chirurgical selon l'une quelconque des revendications 1 - 4, caractérisé en ce qu'il a été confectionné sous forme de structures en filet.
6. Composite chirurgical selon la revendication 5, caractérisé en ce que les structures en filet ont été façonnées en pièces profilées comme des filets courbes et des gouttières.
7. Utilisation d'un composite comprenant une matière choisie parmi les (co)polymères pouvant se résorber, ladite matière contenant des unités constitutives orientées, au moins partiellement fibrillées, qui ont été produites par un étirage de la matière à l'état solide, pour la fabrication d'un dispositif (ou d'une partie d'un dispositif) à employer en chirurgie osseuse, dans lequel au moins la surface dudit dispositif ou de ladite partie a une structure profilée qui comprend lesdites unités constitutives fibrillées.

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